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Density Functional Investigation of Some Decomposition
Routes of Methyl Nitrate

by

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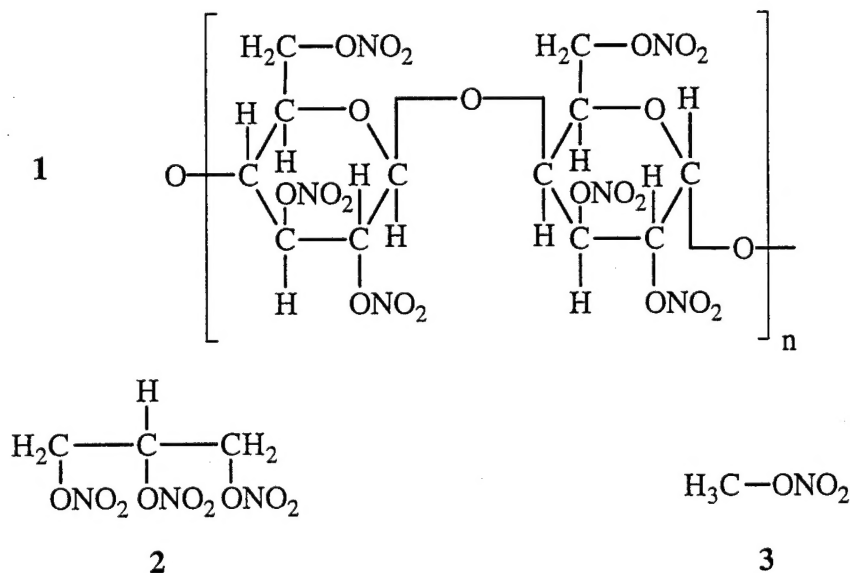
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13. ABSTRACT (Maximum 200 words) Two density functional methods, B3/LYP/6-31+G(d) and B3/PW91/6-31G(d,p) have been used to investigate some possible decomposition pathways for methyl nitrate. Two likely ones were found to be (a) loss of NO ₂ , followed by eventual rearrangement to H ₂ C-OH, and (b) formation of H ₂ C=O and HONO. The initial energy requirement for each process is about 40 kcal/mole, and the second is exothermic, $\Delta H = -16$ kcal/mole of H ₃ C-ONO ₂ . The B3/LYP procedure is found to underestimate the H ₃ CO-NO ₂ and H ₃ C-ONO ₂ dissociation energies by about 7 kcal/mole.				
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1. Introduction

Nitrate esters, such as nitrocellulose (1) and nitroglycerin (2), are one of the major classes of energetic compounds, along with nitramines, nitroaromatics, nitroheterocycles, etc. [1,2]. Nitrocellulose and nitroglycerin, for example, are frequently components of explosive and propellant formulations. Accordingly, any effort to quantitatively analyze and model the combustion behavior of such formulations requires a knowledge of nitrate ester decomposition processes and the associated energetics. As an initial step toward acquiring such data, we have carried out a computational study of several decomposition routes for the simplest nitrate ester, methyl nitrate (3).

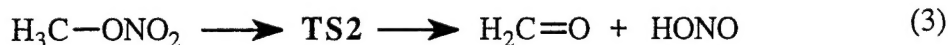
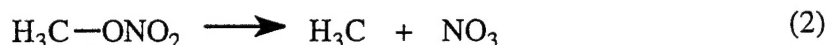
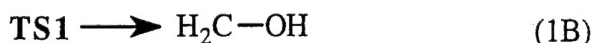
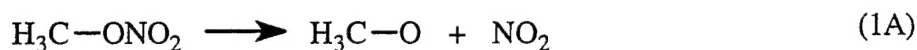


2. Method

We have used two density functional procedures, as incorporated in the program Gaussian 94 [3]: (a) The exchange and correlation functionals were the Becke-3 (B3) and the Lee, Yang and Parr (LYP), respectively [4,5], and the basis set was the 6-31+G(d). (b) The LYP functional was replaced by the Perdew-Wang (PW91) [6], and the 6-31G(d,p) basis set was used.

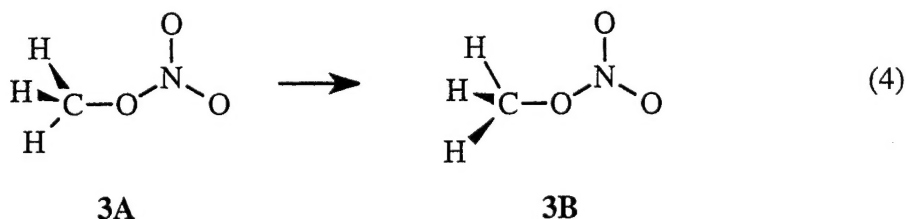
3. Results

We have investigated three possible decomposition pathways, shown as eqs. (1), (2) and (3):



In eqs. (1B) and (3), **TS1** and **TS2** are transition states.

The optimized geometries of the reactants, products and transition states in eqs. (1) - (3) are given in Table 1. The two sets of calculated structures are overall in very good agreement with each other and with the available experimental data. In Table 2 are the total and zero-point energies. We found that the reaction in eq. (3) requires an initial rotation around the C-O bond, as shown in eq. (4):



The geometries and energies of both the ground state **3A** and its conformer **3B** are given in Tables 1 and 2.

In Figure 1 are presented the relative energies at 0 K, including zero-point contributions, of the various stages in the processes shown in eqs. (1), (2) and (3). The corresponding enthalpies at 298 K are given in parentheses [7]. In Table 3 are compared the calculated and experimental enthalpies for the two dissociation processes, eqs. (1A) and (2), and the overall ΔH for the reactions in eqs. (1) and (3).

4. Discussion

The data in Table 3 present an interesting contrast. The overall ΔH for the reactions going through transition states, eqs. (1) and (3), is given reasonably accurately by the B3/LYP procedure, better than by the B3/PW91; however the reverse is true for the dissociation processes, eqs. (1A) and (2), for which the B3/LYP values are too low by about 7 kcal/mole. It has already been noted in the past that the B3/LYP combination tends to underestimate the energy requirements

for the detachment of nitro groups [8,9]. This problem is not overcome by using a larger basis set, as can be seen in Mebel *et al* [8] and as we now confirmed by repeating the B3/LYP calculations for eqs. (1A) and (2) at the 6-311+G(d,p) and 6-311+G(2df,p) levels with no significant improvement. However we have shown earlier [9], for the specific cases of $\text{H}_3\text{C}-\text{NO}_2$ and $\text{H}_2\text{N}-\text{NO}_2$, that better results can be obtained with the B3/PW91 combination, and our present experience reinforces that conclusion, for splitting off ONO_2 as well as NO_2 .

Figure 1 shows that the two computational methods are in good agreement concerning the activation barriers to forming transition states **TS1** and **TS2**. The reliability of B3/LYP activation energies, in particular, has been investigated extensively [10-16]; while an occasional problem is encountered [11], in general the results are quite satisfactory.

With regard to the three methyl nitrate decomposition routes that have been investigated, we conclude therefore that the energy requirement for the first step in eq. (1) is comparable to that for eq. (3). Accordingly both of these processes can be expected to occur, although the second step in eq. (1), leading to **TS1**, has an additional significant energy barrier. It should be noted that eq. (3) is the only one of the three pathways that involves a net release of energy.

5. Conclusions

We find two likely initial decomposition paths for methyl nitrate to be (a) loss of NO_2 , followed by eventual rearrangement to $\text{H}_2\text{C}-\text{OH}$, and (b) formation of $\text{H}_2\text{C}=\text{O}$ and HONO . The initial energy requirement for each process is about 40 kcal/mole, and the second is exothermic, with ΔH (298 K, experimental) = -16 kcal/mole of $\text{H}_3\text{C}-\text{ONO}_2$. From the standpoint of computational methodology, both the B3/LYP and the B3/PW91 density functional procedures were overall effective; however it was again observed that the B3/LYP tends to underestimate dissociation energies involving the loss of NO_2 (and ONO_2 as well).

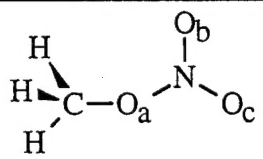
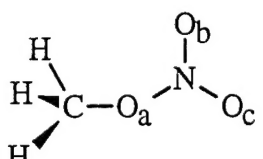
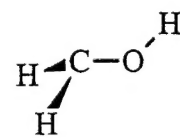
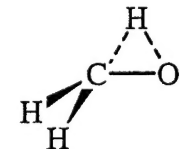
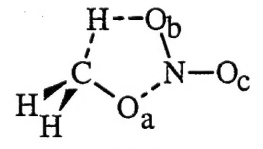
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Table 1. Optimized geometries.^{a,b}

System	Distances, Å		Angles, deg.	
 3A	C-O _a :	1.442, 1.431 (1.437)	C-O _a -N:	113.8, 113.2 (112.72)
	N-O _a :	1.414, 1.404 (1.402)	O _a -N-O _b :	117.5, 117.3 (118.10)
	N-O _b :	1.217, 1.210 (1.205)	O _a -N-O _c :	112.9, 112.8
	N-O _c :	1.208, 1.202 (1.208)	O _b -N-O _c :	129.6, 129.9 (129.52)
 3B	C-O _a :	1.444, 1.433	C-O _a -N:	116.3, 115.8
	N-O _a :	1.421, 1.410	O _a -N-O _b :	118.6, 118.7
	N-O _b :	1.215, 1.209	O _a -N-O _c :	112.0, 111.8
	N-O _c :	1.207, 1.201	O _b -N-O _c :	129.4, 129.5
H ₃ C-O	C-O:	1.371, 1.363		
H ₂ C-O	C-O:	1.209, 1.205 (1.208)	H-C-O:	121.9, 122.4
			H-C-H:	116.3, 115.3 (116.5)
	C-O:	1.371, 1.365	C-O-H:	110.1, 108.8
	O-H:	0.969, 0.963		
H ₃ C	C-H:	1.084 (1.079)	H-C-H:	120, 120 (120)
HO _a NO _b	O _a -H:	0.977, 0.970 (0.958)	H-O _a -N:	103.0, 102.5 (102.1)
	N-O _a :	1.426, 1.411 (1.432)	O _a -N-O _b :	110.9, 110.7 (110.7)
	N-O _b :	1.177, 1.177 (1.170)		
NO ₃	N-O:	1.24, 1.23	O-N-O:	120, 120
NO ₂	N-O:	1.202, 1.198 (1.200)	O-N-O:	134.0, 134.1 (133.8)
 TS1	C-O:	1.389, 1.383	C-O...H:	59.2, 57.9
	C...H:	1.290, 1.260	C...H...O:	67.7, 68.4
	O...H:	1.201, 1.198		
 TS2	C-O _a :	1.288, 1.285	C-O _a ...N:	99.5, 100.0
	N...O _a :	2.054, 1.997	O _a ...N-O _b :	101.8, 102.5
	N-O _b :	1.252, 1.249	N-O _b ...H:	96.4, 96.2
	N-O _c :	1.197, 1.191	C...H...O _b :	145.6, 145.5
	C...H:	1.324, 1.334	H...C-O _a :	96.6, 95.8
	O _b ...H:	1.317, 1.275		

^aFor each distance or angle, the first entry is the B3/LYP result, the second is the B3/PW91.^bExperimental data are in parentheses. They are taken from M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty and A. G. Maki, J. Phys. Chem. Ref. Data **8**, 619 (1979).

Table 2. Calculated total and zero-point energies.

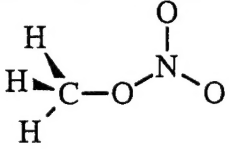
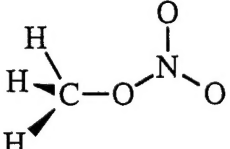
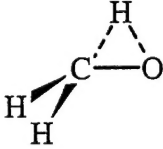
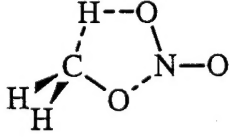
Molecule	Total energy, hartrees		Zero-point energy, kcal/mole	
	B3/LYP	B3/PW91	B3/LYP	B3/PW91
 3A	-320.20538	-320.07402	34.2	34.5
 3B	-320.20248	-320.07132	33.9	34.2
H ₃ C-O	-115.05934	-115.00952	23.0	23.0
H ₂ C-O	-114.50884	-114.45657	16.8	16.8
H ₂ C-OH	-115.06294	-115.01734	23.4	23.6
H ₃ C	-39.84264	-39.82752	18.8	18.7
HONO	-205.70966	-205.62186	12.6	13.0
NO ₃	-280.23253	-280.11270	6.7	6.9
NO ₂	-205.08389	-204.99491	5.5	5.7
 TS1	-114.99963	-114.95524	20.2	20.4
 TS2	-320.13261	-320.00049	29.4	29.8

Table 3. Comparison of calculated and experimental ΔH values, at 298 K, for reactions shown in eqs. (1A), (1), (2) and (3).

Reaction	ΔH , 298 K (kcal/mole of $\text{H}_3\text{C}-\text{ONO}_2$)		
	B3/LYP	B3/PW91	Experimental ^a
1A: $\text{H}_3\text{C}-\text{ONO}_2 \longrightarrow \text{H}_3\text{C}-\text{O} + \text{NO}_2$	33.9	38.4	36.5, ^b 41, ^c 40.7 ^d
1: $\text{H}_3\text{C}-\text{ONO}_2 \longrightarrow \text{H}_2\text{C}-\text{OH} + \text{NO}_2$	32.2	34.3	30.3 ^d
2: $\text{H}_3\text{C}-\text{ONO}_2 \longrightarrow \text{H}_3\text{C} + \text{NO}_3$	74.3	76.4	80.9, ^b 80.7 ^d
3: $\text{H}_3\text{C}-\text{ONO}_2 \longrightarrow \text{H}_2\text{C}=\text{O} + \text{HONO}$	-12.3	-6.8	-15.7, ^b -16 ^c

^aObtained from experimental heats of formation.

^bJ. J. P. Stewart, J. Comp. Chem. 10, 221 (1989).

^cS. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, J. Phys. Chem. Ref. Data 17, suppl. 1 (1988).

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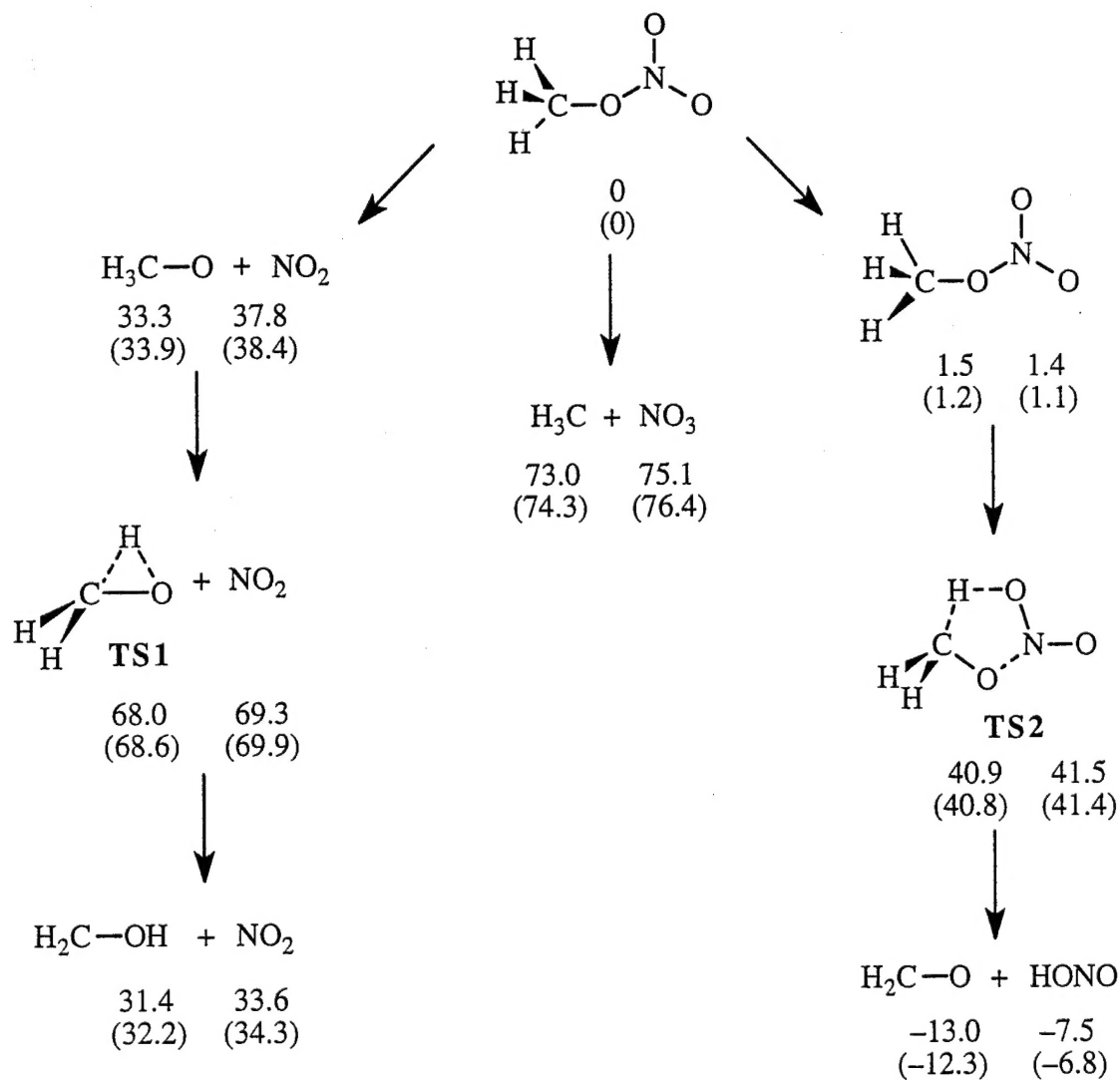


Figure 1. Relative energies at 0 K and relative enthalpies at 298 K (in parentheses) of the various stages in the decomposition processes shown in eqs. (1), (2) and (3). The entries at the left are B3/LYP results; those at the right are B3/PW91. All data are in kcal/mole of $\text{H}_3\text{C}-\text{ONO}_2$.